



# Origin of photocatalytic activity of W/N-codoped TiO<sub>2</sub>: H<sub>2</sub> production and DFT calculation with GGA + *U*

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## ABSTRACT

In the present investigation, to improve photocatalytic efficiency, nitrogen-doped titanium (N-TiO<sub>2</sub>) and tungsten/nitrogen-codoped titanium (W/N-TiO<sub>2</sub>) were prepared by a hydrothermal method and characterized by material analysis and first-principle calculation with generalized gradient approximation (GGA). The highest photocatalytic (PC) efficiency (69%) and TOC removal (32%) for methyl orange were achieved on W0.1%–N1 g–TiO<sub>2</sub> under visible light illumination. Besides, the highest amount of hydrogen produced using W0.1%/N1 g–TiO<sub>2</sub> was 35.2 μmol g<sup>−1</sup> after 2 h of irradiation by visible light. In our simulation models, the GGA + *U* approach (where *U* = 6 and 4 eV) was used for Ti and W atoms, respectively. Density functional theory (DFT) calculation results revealed that a new bond of N–Ti–O linkages formed inside N-TiO<sub>2</sub> was mainly responsible for the narrowed band gap and visible light adsorption. Meanwhile, the intermediate energy states inside the band gap of W/N-TiO<sub>2</sub> were newly formed and resulted in an internal local polarization field between W and N atoms. Consequently, highly effective separation of photogenerated holes and electrons occurred, which was enabled high-performance photocatalysis.

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## 1. Introduction

Hydrogen production as a potential fuel alternative simultaneously addresses energy and environmental problems because hydrogen combustion produces only water molecules [1,2]. An urgent demand for clean and reusable energy brought about by the serious global energy crisis has recently elicited related research on hydrogen evolution approaches, particularly in photocatalytic hydrogen production from solar energy by semiconductor nanomaterials [3,4].

The widely studied TiO<sub>2</sub> photocatalyst is low cost, non-toxic, and chemically stable. TiO<sub>2</sub> is also used for waste remediation, in solar cells, optoelectronic devices, and water splitting [5–10]. However, the wide band gap of TiO<sub>2</sub> (3.2 eV for anatase TiO<sub>2</sub>) hinders its photocatalytic applications. Thus, modification of the band gap of TiO<sub>2</sub> should be lessened so that the absorption edge can be shifted to the visible light region. Doping is one of the promising approaches to accomplish this task [11,12]. However, this strategy can also improve the interfacial charge transfer and lower the

photo generated electrons–holes recombination rate result in poor PC activity [13]. Therefore, at recently, TiO<sub>2</sub> codoped with transition metal and nonmetal such as V/N [14], Fe/N [15], Sn/N [16], and S/N [17] is attracting considerable interest.

Among these materials, nitrogen (N) [18,19] is one of the most used doping nonmetal elements because of its reasonable ionic radius, which is similar to that of O. Based on DFT calculations, the N doping introduces a new energy state in band gap of TiO<sub>2</sub>, reducing the photon energy required of the creation of photo generated electron–hole pairs, which is ascribed to N 2p states can effectively merge with O 2p states [20]. Meanwhile, tungsten (W) is considered to be one of the best transition metal elements for improving the photocatalysis (PC) activity of TiO<sub>2</sub> [21]. Due to the high valent value of W<sup>6+</sup>, W(VI) acts as electron traps inside the lattice of W doped TiO<sub>2</sub>, which prevents the recombination of photo generated electron–hole pairs as well as enlarges the absorption edge of excitation light to visible range [22]. However, for W/N-TiO<sub>2</sub>, due to the presence of W and N, the energy states of them will be affected together, resulting in high PC performance of W/N-TiO<sub>2</sub> which might be caused by some special reasons. Therefore, a systematic and comprehensive mechanism, as well as a support mechanism for codoped TiO<sub>2</sub> system, must be identified.

Recently, first-principle calculations were conducted for N or W doped TiO<sub>2</sub>. Asahi et al. [23] pointed out that the high PC performance of N-TiO<sub>2</sub> is ascribed to the narrowing of band gap by mixing

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O 2p and substitutional N 2p states. Diwald et al. [24] thought that interstitial N species doped in  $\text{TiO}_2$  could also narrow the band gap. On the other hand, for W doped  $\text{TiO}_2$ , Marquez et al. [25] reported that the short distance W–Ti bond is responsible for the narrowed band gap. However, only few reports discussed the theory of high PC activity of W/N– $\text{TiO}_2$  accompanying with real experiments.

Here in, we present our results on the synthesis of  $\text{TiO}_2$ , N– $\text{TiO}_2$  and W/N– $\text{TiO}_2$  prepared by hydro-thermal method. These catalysts were characterized by a serial of equipments. Their photocatalytic properties were conducted by the photo degradation of methyl orange (MO) and the production of  $\text{H}_2$  under visible light. GGA + *U* calculations were conducted to further illustrate the mechanism of PC activity of doped or codoped  $\text{TiO}_2$  systems.

## 2. Experimental

### 2.1. Reagents

Titanium isopropoxide, sodium tungstate, urea, sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), anhydrous ethanol, acetone, hydrochloric acid and MO were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Coumarin was purchased from Sigma-Aldrich. All chemicals were of analytical grade. All solutions were prepared with deionized water.

### 2.2. Preparation of catalysts

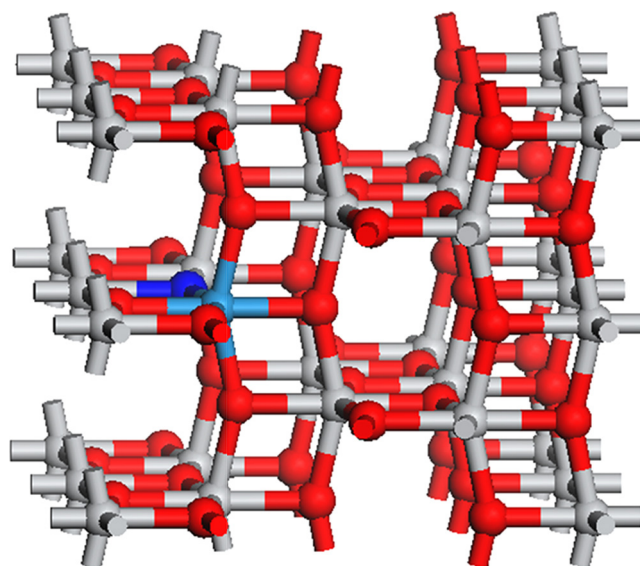
$\text{TiO}_2$  was prepared by hydrothermal method. In brief, about 10 mL of titanium isopropoxide was added into 30 mL of an ethanolic solution under vigorous stirring and then labeled as solution A. About 1 mL of hydrochloric acid and 1 mL of deionized water were added into 10 mL of an ethanol solution, which was labeled as solution B. Then, solution B was slowly added to solution A under vigorous stirring. After 1 h stirring, the mixed solution was transferred to a Teflon-lined autoclave at  $110^\circ\text{C}$  for 12 h. The products were harvested by centrifugation and then washed with deionized water several times to remove dissoluble ionic impurities. Finally, as-prepared catalysts were calcined at  $600^\circ\text{C}$  for 2 h, denoted as  $\text{TiO}_2$ . On the other hand, after the solution B added into solution A, and the desired concentration of urea or (and) sodium tungstate was added into the mixed solutions and follows the rest of process similar to produce  $\text{TiO}_2$ , the N doped  $\text{TiO}_2$  (N– $\text{TiO}_2$ ) or W/N codoped  $\text{TiO}_2$  (W/N– $\text{TiO}_2$ ) samples were obtained.

### 2.3. Characterization

(TEM) Sirion 200 FSEM (FEI, The Netherlands) and H-600 PV9100 HRTEM (HITACHI, Japan) were employed for catalysts morphology characterization and crystal lattice, respectively. The phase detection and analysis were conducted on XRD (X'Pert PRO, PANalytical B.V., The Netherlands). XPS analysis was performed on a 5300 ESCA instrument (Perkin-Elmer PHI Co., USA). The UV–visible diffuse reflectance spectra were conducted by a UV–visible spectrophotometer equipped with CARY-50 Probe (USA). The fluorescence spectra were recorded on a RF-5301PC (SHIMADZU, Japan) fluorometer. The total organic carbon was determined by TOC-VCSH analyzer (Shimadzu, Japan).

### 2.4. Evaluation of photocatalytic activity

The photocatalytic activity of all as-prepared samples was evaluated by degrading methyl orange (MO; 5 mg/L) aqueous solution under 300 W Xe lamps through a UV-cutoff filter (<400 nm) as visible light at ambient temperature. The visible light intensity, measured with a visible-light radiometer (Model: FZ-A, China), was



**Fig. 1.** Additional W and N positions located in the  $2 \times 2 \times 1$  anatase supercell for calculations (the colors gray, red, blue and pistachio indicate O, Ti, N and W, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$125 \text{ mW cm}^{-2}$ . For the photocatalysis (PC) system, 50 mg of catalyst particle was dispersed in 100 mL of MO aqueous solution. The concentration of MO was analyzed with a UV–visible spectrometer (WFZ UV-2000, China). For absorbance measurement, 3 mL of sample was taken out from the photoreactor at given time intervals after centrifugation. The equipment for PC procedure-based MO degradation was fabricated according to the previous study [26]. The formation of  $\bullet\text{OH}$  radicals was monitored by using coumarin as a fluorescence probe. The fluorescence method is a very specific detector with high sensitivity for the quantitative measurement of  $\bullet\text{OH}$  radicals, in which coumarin easily reacts with  $\bullet\text{OH}$  to form highly fluorescent 7-hydroxy coumarin (umbelliferone) [27]. The absorbance of umbelliferone was recorded based on fluorescence spectra in the absorption range from 400 to 550 nm, using 350 and 455 nm as the excitation and emission wavelengths, respectively.

### 2.5. The evolution of hydrogen production

The experiments were conducted in an aqueous suspension of catalyst with ethanol as the sacrificial agent under visible light. In brief, photocatalytic hydrogen production reactions were performed in a 50 mL glass reactor. Typically, 50 mg of the catalyst was suspended in 20 mL of  $\text{H}_2\text{O}$  containing 20 mL of ethanol illuminated with visible light. In order to eliminate dissolved oxygen, the suspension was degassed for 30 min with  $\text{N}_2$  stream prior to visible light illumination. The amount of  $\text{H}_2$  produced was measured by a gas chromatogram (Agilent, 4890D) equipped with a TCD detector.

### 2.6. Theoretical calculations

All calculations were performed using density functional theory (DFT) based on CASTEP software package within the GGA using Materials Studio v5.5 through a plane-wave pseudopotential approach [28]. The doped systems were constructed from a relaxed anatase  $\text{TiO}_2$  supercell ( $2 \times 2 \times 1$ ) containing 48 atoms (16 Ti and 32 O atoms), as shown in Fig. 1. N-doped  $\text{TiO}_2$  (N– $\text{TiO}_2$ ) was modeled by single substitution of N for one O atom per supercell. W/N-codoped  $\text{TiO}_2$  replaced one Ti and one O atom per supercell. An ultrasoft pseudopotential was used for geometric optimizations. The electron wave function was expanded in the plane waves up

to a cutoff energy of 400 eV, and a  $2 \times 2 \times 1$  Monkhorst–Pack  $k$ -point mesh was used to calculate electronic property. Standard local density approximation (LDA+ $U$ ) was performed to calculate electronic and optical properties on the structures optimized by GGA PBE method [29,30]. To describe Ti 3d states, the LDA+ $U$  approach (where  $U=6$  and 4 eV, respectively, for Ti and W) was used. The use of  $U$  to properly describe the electronic states of d shells was introduced [31]. Mechanical equilibrium was achieved through conjugate gradient minimization of the total energy with a tolerance level of  $2 \times 10^{-6}$  eV, the forces with a tolerance level of  $0.05 \text{ eV } \text{\AA}^{-1}$ , and the atomic position with a tolerance level of  $0.002 \text{ \AA}$ . The nature of the incorporated N and its loading place in the  $\text{TiO}_2$  lattice are still under debate. Here, we chose a reasonable loading place based on another report [32].

### 3. Results and discussion

#### 3.1. Characterization of catalysts

The shape and lattice of particles were examined by FSEM and HRTEM (Fig. 2).  $\text{TiO}_2$  exhibited spherical shape and uniformity in

particles with a large average size of  $1 \mu\text{m}$  (Fig. 2A). The HRTEM image (Fig. 2B) indicated that the lattice spacing was ca.  $0.332 \text{ nm}$ , corresponding to the (101) facet on  $\text{TiO}_2$ . After adding N (Fig. 2C), more minute particles were aggregated. The change in morphology may be mainly attributed to urea acting as a surfactant in the thermal treatment, which can inhibit the growth of  $\text{TiO}_2$  surface [33]. In the hydrothermal reaction, a semiconducting organic layer may be formed [34], and this layer is chemically bound to  $\text{TiO}_2$  because of the surface  $-\text{OH}$  groups on  $\text{TiO}_2$ , similar to the case of silica [35]. Reduced particle size is generally beneficial for PC because it leads to quadratic growth of the specific surface area and reactive sites. In addition, the presence of urea enabled the lattice spaces to increase to ca.  $0.346 \text{ nm}$  (Fig. 2D), indicating that the successful doping of N penetrated the  $\text{TiO}_2$  lattice. In the case of W/N- $\text{TiO}_2$  particles, the morphology was similar to that of N- $\text{TiO}_2$ , as shown in Fig. 2E. However, the morphology obtained a higher value of lattice space (ca.  $0.364 \text{ nm}$ ) (Fig. 2F), which may be due to the addition of W resulting in the formation of an O–W–N bond. Given the presence of a new bond, the bond lengths and angles between Ti–O, O–Ti–O, or Ti–O–Ti bonds inside W/N- $\text{TiO}_2$  may be affected compare with  $\text{TiO}_2$ , indicating high PC performance. This topic is discussed later.

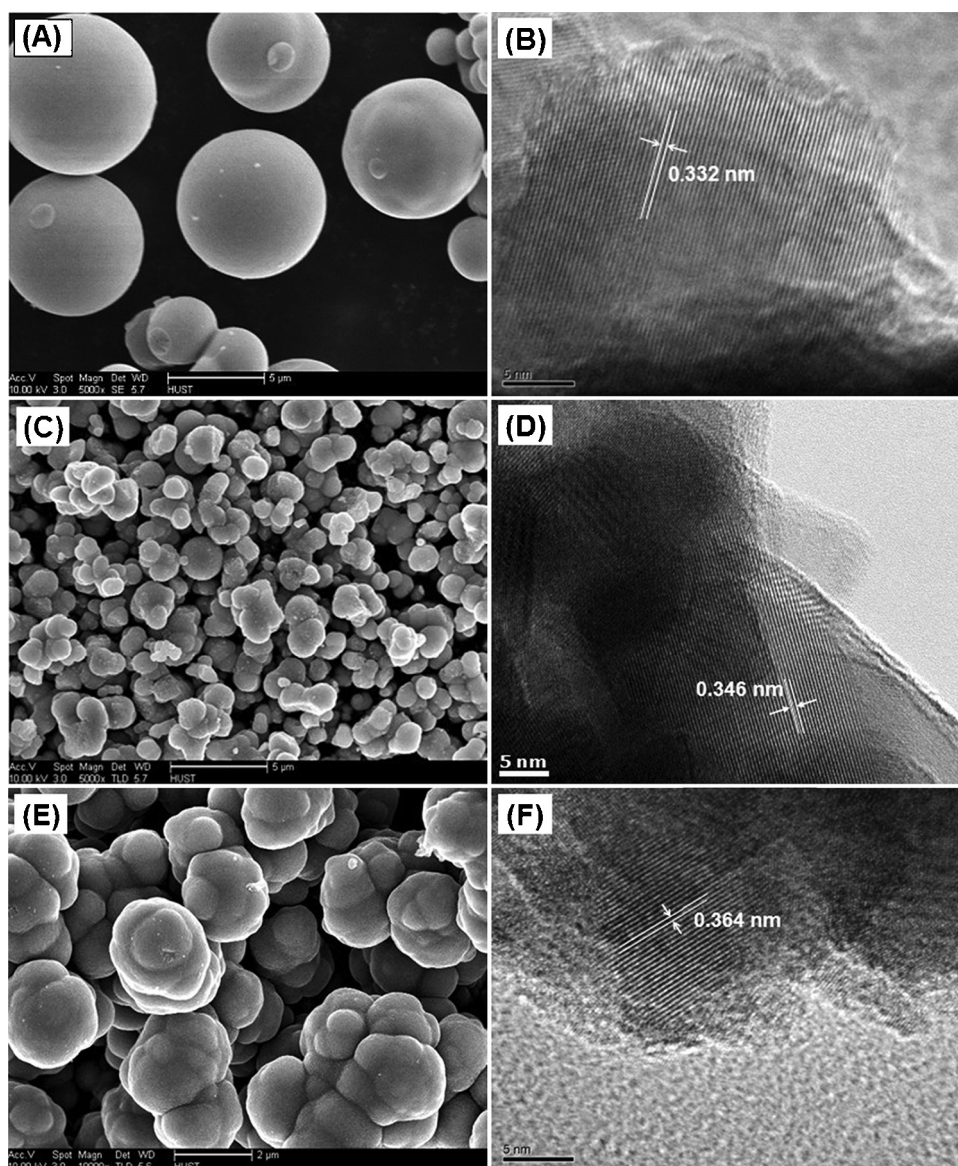


Fig. 2. FSEM images of (A)  $\text{TiO}_2$ , (C) N1 g- $\text{TiO}_2$ , and (E) W0.1%-N1 g- $\text{TiO}_2$  particles. HRTEM images of (B)  $\text{TiO}_2$ , (D) N1 g- $\text{TiO}_2$ , and (F) W0.1%-N1 g- $\text{TiO}_2$  particles.



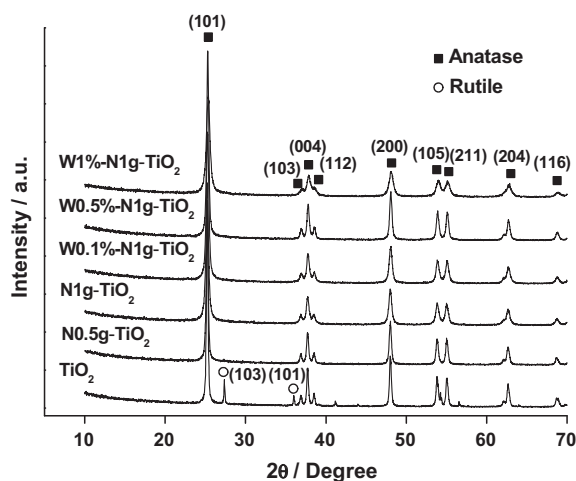


Fig. 3. XRD patterns of catalysts calcined at 600 °C.

Fig. 3 shows the crystal phase of different catalysts. The XRD peaks at  $2\theta = 27.4$  (R 103) and  $36.1$  (R 101) are the characteristic peaks of the rutile crystal phase [36] that appear in  $\text{TiO}_2$ . The other peaks of samples can be readily indexed to pure anatase phase, consistent with the reported values (JCPDS no. 21-1272). Notably, no visible peaks corresponding to N or W were found after doping, except those of the anatase phase. Thus, the dopant was added into the  $\text{TiO}_2$  lattice. According to the Scherrer equation

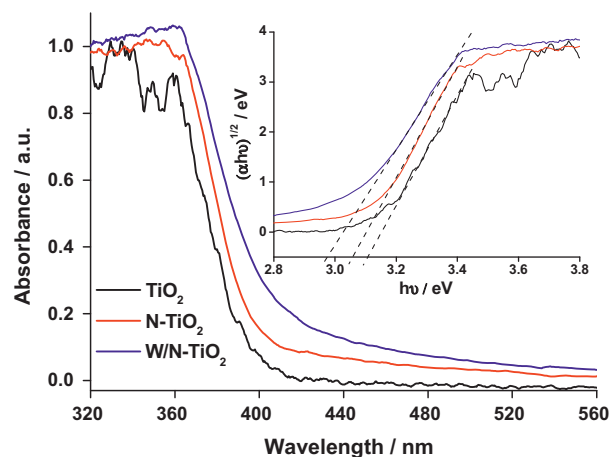


Fig. 4. UV-visible diffuse reflectance spectra of  $\text{TiO}_2$ ,  $\text{N1g-TiO}_2$  and  $\text{W0.1\%-N1g-TiO}_2$ . The inset shows the plots of  $[\alpha h\nu]^{1/2}$  versus  $h\nu$  for band-gap energies.

[37], the average crystalline sizes of these catalysts can be calculated from the major diffraction peak (101) of the anatase phase, as listed in Table 1. The crystalline sizes of  $\text{TiO}_2$ ,  $\text{N0.5g-TiO}_2$ , and  $\text{N1g-TiO}_2$  were 22.6, 20.8, and 20.1 nm, respectively. Hence, a large amount of N doping can slightly suppress the growth of  $\text{TiO}_2$ . By contrast, the crystalline sizes of W/N-codoped samples were larger than those of pure  $\text{TiO}_2$  and  $\text{N-TiO}_2$ , indicating that the doping of W can remarkably improve the growth of  $\text{TiO}_2$ . Based on Bragg's

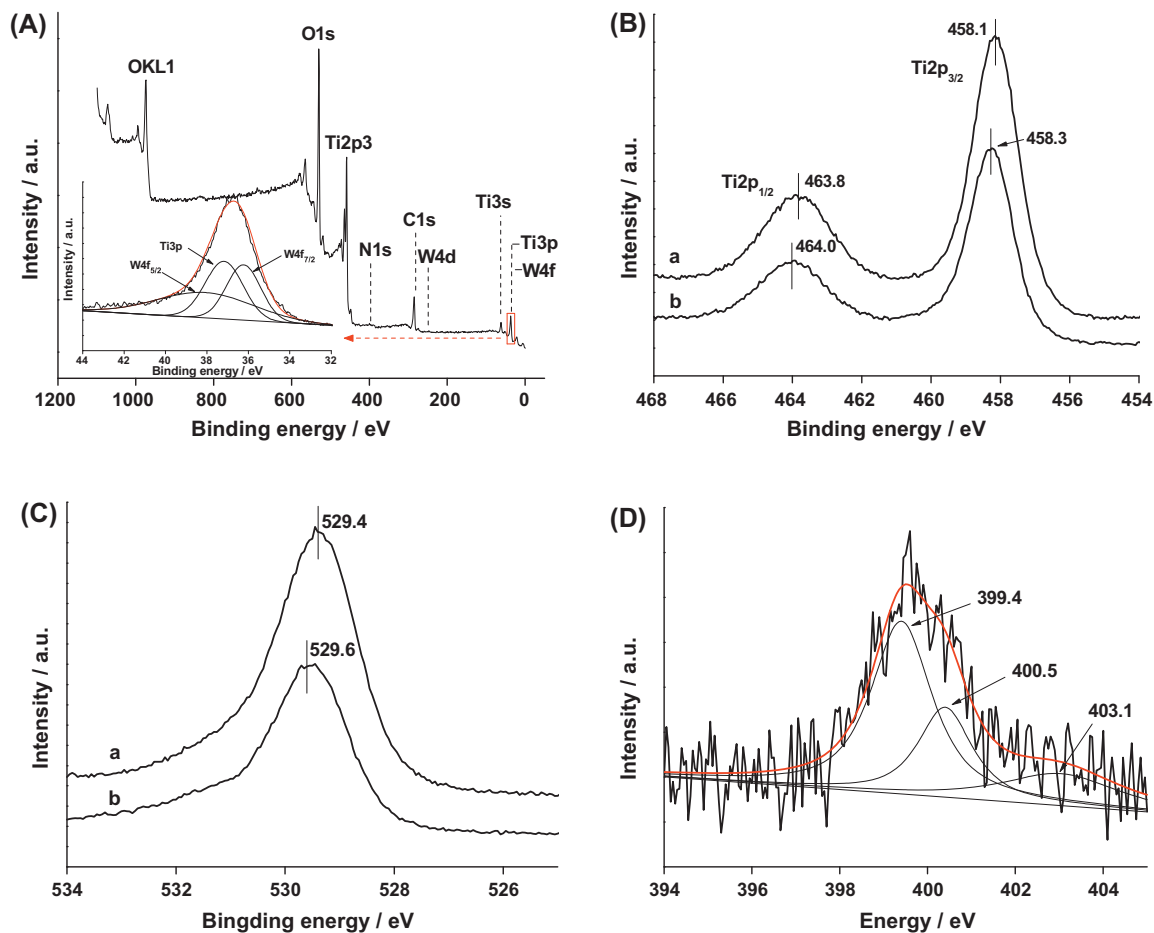


Fig. 5. (A) XPS global spectra of W/N- $\text{TiO}_2$ , and the inset of (A) is the XPS spectra of W4f. XPS spectra of (B) Ti 2p and (C) O 1s peaks, as well as of (a)  $\text{TiO}_2$  and (b) W/N- $\text{TiO}_2$ , respectively. (D) XPS spectra of N 1s peak of W/N- $\text{TiO}_2$ .

**Table 1**  
Physical characteristics of catalysts.

Sample	Crystallite size (nm)	Lattice parameter (Å)	
		<i>a</i> = <i>b</i>	<i>c</i>
TiO <sub>2</sub>	22.6	3.7725	9.5178
N0.5 g-TiO <sub>2</sub>	20.8	3.7622	9.5332
N1 g-TiO <sub>2</sub>	20.1	3.7643	9.5378
W0.1%-N1 g-TiO <sub>2</sub>	25.3	3.7622	9.6223
W0.5%-N1 g-TiO <sub>2</sub>	26.5	3.7642	9.6321
W1%-N1 g-TiO <sub>2</sub>	26.9	3.7702	9.6331

law ( $2d_{hkl} \sin \theta = n\lambda$ ) [38] and the formula for a tetragonal unit cell ( $1/(d_{hkl})^2 = (h^2 + k^2)/a^2 + l^2/c^2$ ), the lattice parameters were calculated and are listed in Table 1. The lattice values along the *c*-axis increased with W doping, indicating that the doped W ion may be present in a hexed-oxidation state, which can partially replace Ti<sup>4+</sup> to form a Ti–O–W bond [39]. Several similar phenomena have been reported in metal doping systems [40,41].

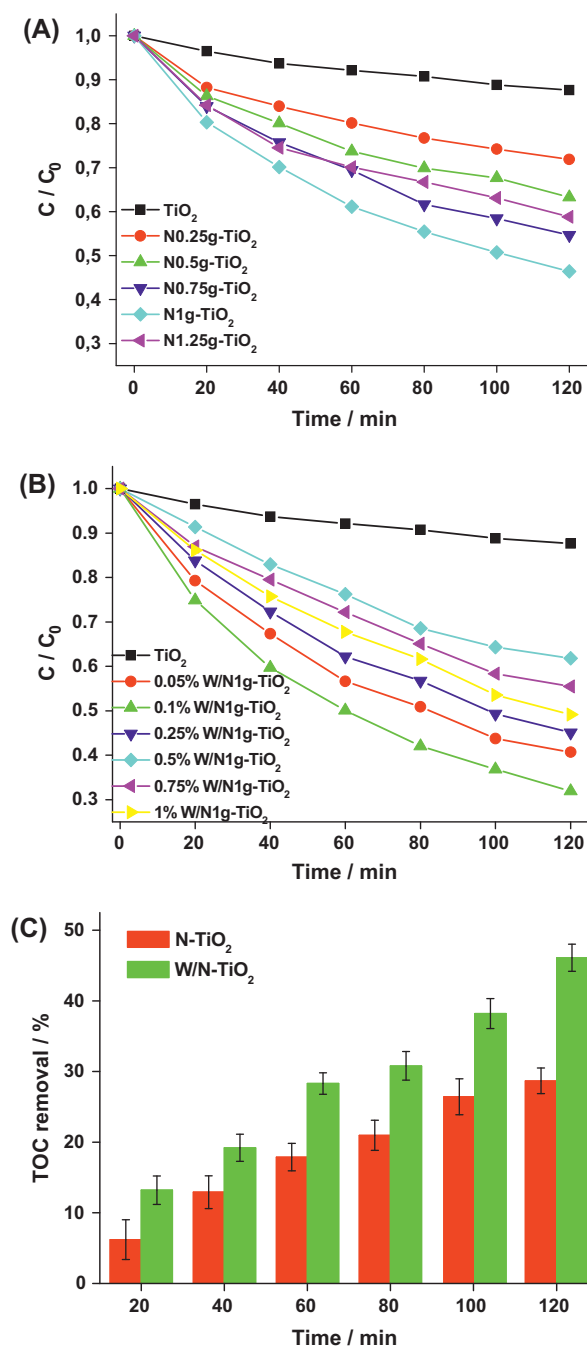
The optical properties of materials were altered after metal doping [42]. Fig. 4 compares the UV–visible absorption spectra of TiO<sub>2</sub>, N-TiO<sub>2</sub> and W/N-TiO<sub>2</sub>. The inset in Fig. 4 shows the plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$ . The vertical segment of the spectra is extended to intersect the  $h\nu$  axis (*x*-axis) to obtain the band gap ( $E_g$ ) values of catalysts. Afterwards, the diffusive reflectance measurements were converted into the equivalent absorption coefficient by the Kubelka–Munk [43] function as follows:

$$\alpha h\nu = C(h\nu - E_g)^2 \quad (1)$$

$$h\nu = \frac{1240}{\lambda} \quad (2)$$

where  $\alpha$  is optical absorption coefficient near the absorption edge for indirect interband transitions, which can be replaced with the absorbance of diffuse reflectance UV–visible, *C* is the absorption constant for an indirect transition ( $C = 1$ ),  $h\nu$  is the photon energy,  $\lambda$  is the wavelength (nm), and  $E_g$  is the bandgap energy (eV). The band gap of TiO<sub>2</sub> (3.16 eV) is narrowed to 3.04 and 2.96 eV for N-TiO<sub>2</sub> and W/N-TiO<sub>2</sub>, respectively. In the case of N-TiO<sub>2</sub>, a visible light absorption shoulder ranging from 380 to 440 nm was obtained from the interstice because of the introduction of new localized states close to the VB edge [44]. Meanwhile, for several kinds of transition metal elements, the cation with d<sup>10</sup> electronic configurations can introduce occupied d or s states into the VB. Hybridization of these d/s states with O 2p states contributes to an upshift of the top VB and narrows the band gap. Therefore, in the case of W/N-TiO<sub>2</sub>, continuous adjustment of the ratios of N 2p states to O 2p states in the VB and W 4d to Ti 4d states in the conduction band (CB) refabricate optimal band structures resulting in the narrowest band gap.

To evaluate the chemical composition and bonding states among elements, XPS was carried out, and the global range XPS spectra are shown (Fig. 5). The main peaks of Ti, O, W and N can be detected. The inset in Fig. 5A is the XPS spectra of W 4f containing Ti 3p. The peak that came out at 36.7 can be attributed to the presence of W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub> located at 36.2 and 38.1 eV, respectively. Meanwhile, the other peak at 37.1 eV resulted from the Ti 3p state [45]. Fig. 5B shows that the Ti-2p<sub>3/2</sub> and Ti-2p<sub>1/2</sub> peaks of TiO<sub>2</sub> were at 458.1 and 463.8 eV, respectively. However, the peaks for W/N-TiO<sub>2</sub> shifted to a higher binding energy at 458.3 and 464.0 eV for Ti-2p<sub>3/2</sub> and Ti-2p<sub>1/2</sub>, respectively. The peak shift indicated that the formation of Ti–N and/or Ti–O–W bands were mainly due to the partial replacement of O and Ti in TiO<sub>2</sub> by N and W, respectively [46]. Fig. 5C shows that the O 1s peak of TiO<sub>2</sub> shifted from 529.4 to 529.6 eV compared with those of W/N-TiO<sub>2</sub>. The shift can also be attributed to the substitution of O<sup>2-</sup> by N<sup>3-</sup> in the TiO<sub>2</sub> crystal and the formation of new O–Ti–N bond types [47]. Fig. 5D shows a broad peak extending from 397 to 404 eV for

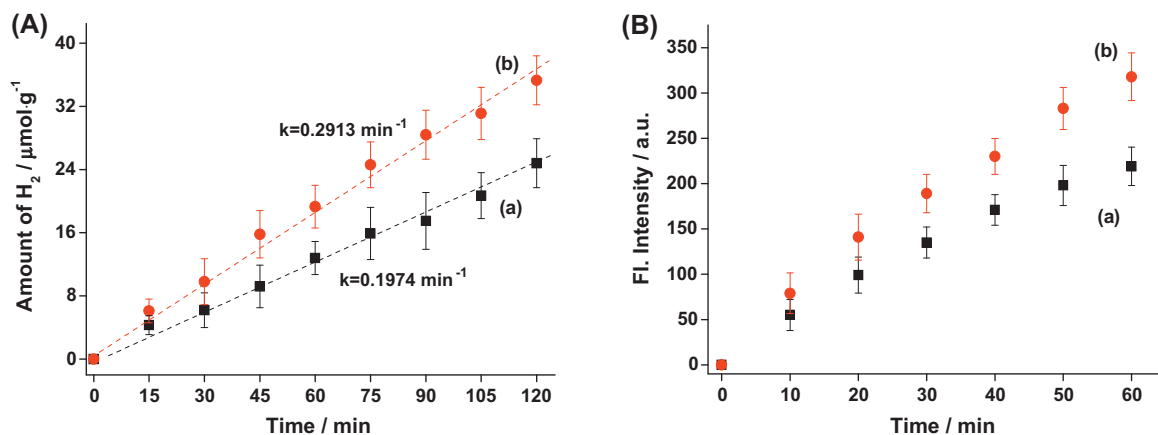


**Fig. 6.** PC degradation efficiency on (A) N-TiO<sub>2</sub> and (B) W/N-TiO<sub>2</sub>. (C) TOC removal of MO by N1 g-TiO<sub>2</sub> and W0.1%-N1 g-TiO<sub>2</sub>.

W/N-TiO<sub>2</sub>. This peak was fitted using soft XPS peak fit to three very distinct peaks at 399.4, 400.5, and 403.1 eV. The peak at 399.4 eV can be attributed to the substitution of anionic N<sup>3-</sup> in O–Ti–N linkages [48]. The second peak (400.5 eV) may be due to O–Ti–N linkage or some surface oxidation linkages resulting in the high PC activity of N-TiO<sub>2</sub> [49]. The third peak located at 403.1 eV can be attributed to chemisorbed N-containing species [50].

### 3.2. Photocatalytic activity of catalysts

The PC activities of samples were first evaluated by the degradation of MO under visible light, as shown in Fig. 6. Fig. 6A shows increased PC efficiency of MO with increased N concentration. N1 g-TiO<sub>2</sub> achieves the best PC efficiency at 55%, which



**Fig. 7.** (A) Time course of H<sub>2</sub> evolution and (B) fluorescence spectra of umbelliferone in 1 mM coumarin solution in the presence of (a) N1 g-TiO<sub>2</sub> and (b) W0.1%-N1 g-TiO<sub>2</sub>, respectively.

is almost four times higher than that of TiO<sub>2</sub> (13%). However, with 1.25 g of N, the PC efficiency decreased to 42%. An appropriate amount of impurity (N) inside the lattice of TiO<sub>2</sub> formed a new internal energy level to separate photogenerated holes and electrons. However, too much dopants doped on TiO<sub>2</sub> would accumulate on the interstice or vacancy of lattice to form a new recombination center, and it would also largely reduce the exposed surface of catalysts and thereby decrease the chance for the photogenerated holes to oxidize pollutant [51]. Thus, 1 g of N was deemed the best concentration to conduct future research. For different W/N-TiO<sub>2</sub> samples (Fig. 6B), the highest PC efficiency (69%) was achieved on W0.1%-N1 g-TiO<sub>2</sub>. Besides, the high PC activity of W0.1%-N1 g-TiO<sub>2</sub> was also proven by TOC removal (32%), which was two times higher than that of N1 g-TiO<sub>2</sub> (15%), as shown in Fig. 6C. Similarly, too much of W in codoped samples resulted in lower PC efficiency because the new hole-electron recombination centers will catch the photo-generated holes.

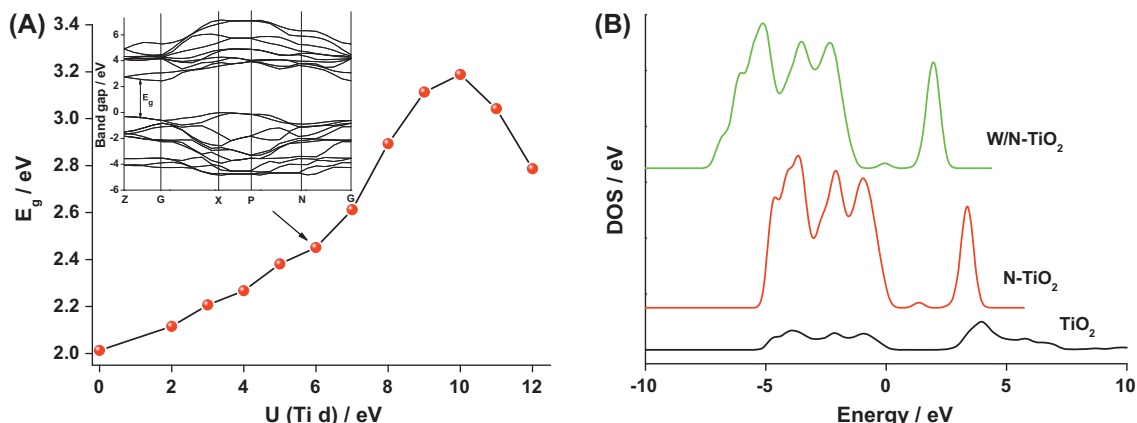
PC H<sub>2</sub> evolution experiments were conducted to further understand catalytic ability of samples. Fig. 7A shows the quantity of H<sub>2</sub> evolution with various catalysts as a function of time course through visible light irradiation. The lifetime of photo-induced electron holes can be improved with reagents reacting irreversibly with photo-induced holes or photogenerated oxygen. Thus, the hydrogen evolution rate increased because of the reactions between photogenerated electrons and water [52,53]. W0.1%-N1 g-TiO<sub>2</sub> comprised 35.1 μmol g<sup>-1</sup> H<sub>2</sub> after 2 h of irradiation, which was much higher than that of N1 g-TiO<sub>2</sub> (24.8 μmol g<sup>-1</sup>). A higher

hydrogen production rate of 0.2913 μmol min<sup>-1</sup> was also obtained from W0.1%-N1 g-TiO<sub>2</sub>, which was almost 1.47 times that of N1 g-TiO<sub>2</sub> (0.1974 μmol min<sup>-1</sup>). Conversely, almost no H<sub>2</sub> evolution was detected from TiO<sub>2</sub> even after 2 h of irradiation (not shown).

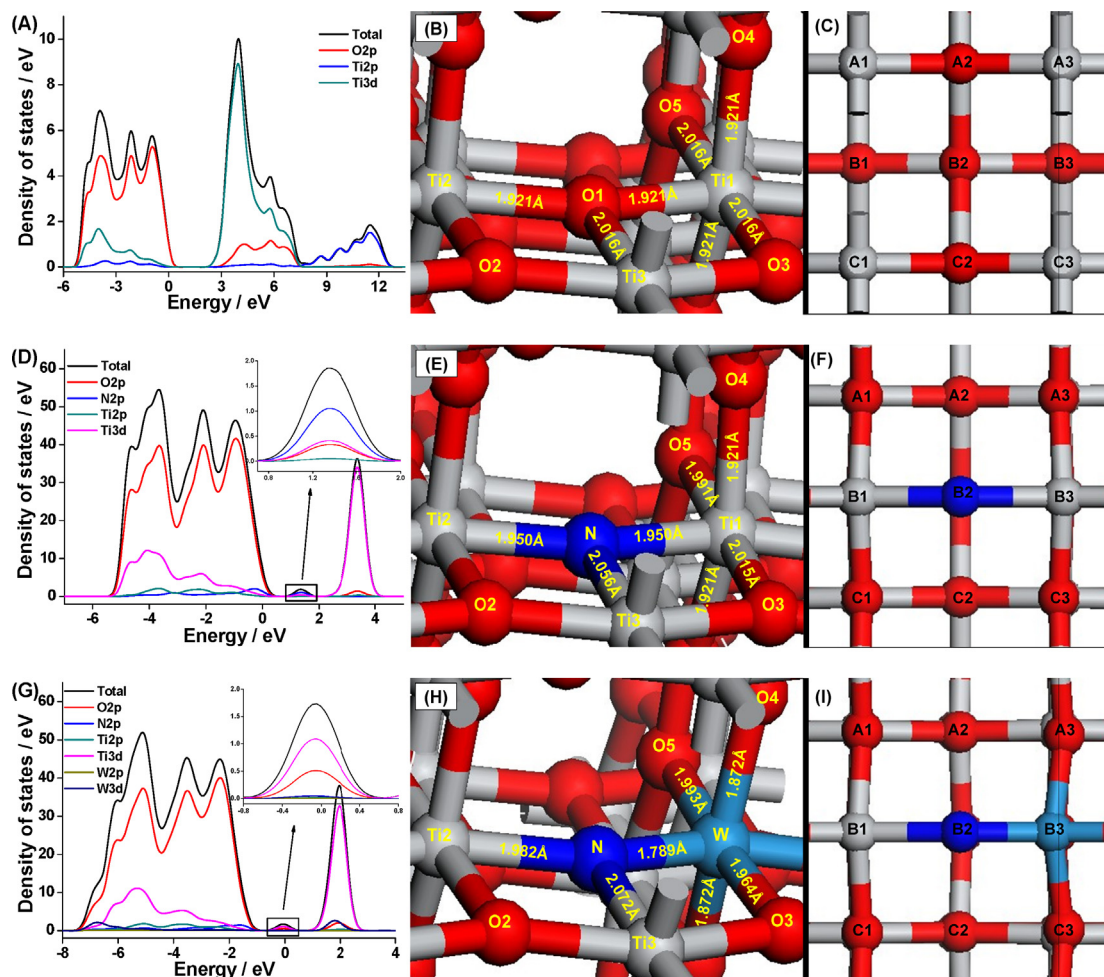
The PC activity of samples was further confirmed by the detection of •OH radicals. Fig. 7B shows changes in the PL spectra of umbelliferone generated in 0.1 mM coumarin solution by visible light irradiation as a function of irradiation time. The PL intensity was directly related to the amount of •OH radicals [54]. The PL intensity produced by W0.1%-N1 g-TiO<sub>2</sub> was much higher than that of N1 g-TiO<sub>2</sub> indicating that the former had the highest PC activity, which well agreed with PC results. Meanwhile, weak PL intensity was observed for the TiO<sub>2</sub> because it was not activated by visible light (not shown).

### 3.3. Analysis of DFT calculations

GGA+*U* can partially correct the band gap relative to experimental value and is usually used to deal with a strongly correlated system [55]. Generally, the main effect of *U* is to change the location of the impurity energy state inside band gap. However, the relative energies among possible positions of electron localization remain unchanged while different *U* values are used [56]. So, we thus focus on results using a *U* value of 6 eV. The relationship between the band gap of TiO<sub>2</sub> and value of *U* (on Ti-d) was calculated and is shown in Fig. 8A. The inset in Fig. 8A is the band gap of TiO<sub>2</sub> (2.45 eV), and the *U* value is 6 eV. The density of state (DOS) of catalysts was



**Fig. 8.** Band gaps ( $E_g$ ) of TiO<sub>2</sub> calculated based on different *U* (Ti-d state) parameters within the LDA+*U* program. The inset is the band gap of TiO<sub>2</sub>, and *U* (Ti-d state) = 6.



**Fig. 9.** PDOS of (A)  $\text{TiO}_2$ , (D)  $\text{N-TiO}_2$  and (G)  $\text{W/N-TiO}_2$ . Structure around the dopant site for (B)  $\text{TiO}_2$ , (E)  $\text{N-TiO}_2$  and (H)  $\text{W/N-TiO}_2$ . Atomic structure (showing only one plane) for (C)  $\text{TiO}_2$ , (F)  $\text{N-TiO}_2$  and (I)  $\text{W/N-TiO}_2$ . The colors gray, red, blue and pistachio denote O, Ti, N and W, respectively. The position of atoms is also marked with numbers.

calculated to compare the modifications in electronic structure of the different doped systems, as shown in Fig. 8B. The band gap of  $\text{TiO}_2$  was found to be nearly ca. 2.2 to 2.5 eV [55], which was much smaller than the experimental value because of the shortcomings of the exchange–correction function in describing excited states [57,58]. Fig. 8B shows that the calculated band gap of  $\text{TiO}_2$ ,  $\text{N-TiO}_2$  and  $\text{W/N-TiO}_2$  were 2.45, 1.56 and 1.14 eV, respectively. Interestingly, for  $\text{N-TiO}_2$ , the internal energy level came out, resulting from charge hybridization between N 2p, O 2p and Ti 3p (as proven later). Cheng et al. [44] pointed out that interstitial  $\text{N-TiO}_2$  result in a visible light absorption shoulder from 380 to 500 nm because of the introduction of localized states near the VB edge. Under irradiation, photogenerated electrons can easily transfer from the VB to intermediate states, and electrons in the newly formed states can subsequently transit to the CB when excited [59]. These phenomena are responsible for the visible light-excited PC activity of  $\text{N-TiO}_2$ . Similarly, for  $\text{W/N-TiO}_2$ , another state is located inside the band gap of  $\text{W/N-TiO}_2$ , which is mainly contributed by the hybridization of electrons between Ti 3p and O 2p. Generally, these intermediate energy levels pave the way for high PC performance [60]. To clearly understand what happened inside these lattices, projected DOS (PDOS) and bond length were calculated.

The PDOS of catalysts are shown in Fig. 9. The PDOS in Fig. 9A revealed that for  $\text{TiO}_2$ , the O 2p states dominate the top VB, and the Ti 3d states dominate the bottom of the CB. After the addition of N in  $\text{N-TiO}_2$  (Fig. 9D), O atoms still occupied the VB. However, a new

interior energy state was observed in the middle of the band gap mainly dominated by N 2p states (inset of Fig. 9D). Thus, the state is localized in the band gap, resulting in the narrowing of the maximum band value compared with undoped  $\text{TiO}_2$ . Considering that the atomic radius of N was slightly larger than that of O,  $\text{N-TiO}_2$  at the vacant oxygen position resulted in the distortion of octahedral  $\text{TiO}_4$  units [61]. Therefore, the strong orbital interaction between N and neighboring O atoms in an octahedral unit led to the separation of  $[\text{Ti } 3d + \text{O}_2 \text{ p}\pi]$  hybrid states [62]. Consequently, vicinal Ti and O atoms simultaneously interacted and partly overlapped with electron orbits, resulting in changes in bond length and bond angle. Fig. 9B and E shows the geometry around the dopant site in anatase for  $\text{TiO}_2$  and  $\text{N-TiO}_2$ , respectively. The N–Ti1 bond distance of  $\text{N-TiO}_2$  (1.950 Å) increased compared with that of O1–Ti1 in the case of  $\text{TiO}_2$  (1.921 Å). Meanwhile, the transformation of bond length changed bond angles. Fig. 9C and F shows that O–Ti–N, which is mainly responsible for absorption in the visible region of  $\text{N-TiO}_2$  [23,62], caused the bond angle of  $\text{N-TiO}_2$  ( $\angle \text{A3B3B2}$ ) to be narrowed to  $89.38^\circ$  compared with that of O–Ti–O ( $90^\circ$ ).

In the case of  $\text{W/N-TiO}_2$ , the PDOS is shown in Fig. 9G. The top VB and bottom CB are still governed by O 2p and Ti 3d, respectively. However, the VB edge shifted from 0.38 to  $-0.98$  eV because of the presence of W, which drastically affected the Ti unoccupied DOS and subsequently influenced Ti–N bonds. The CB edge also moved from 2.37 to 0.96 eV [63]. In addition, the newly formed intermediate energy state was not mainly charged by N 2p, as shown in the



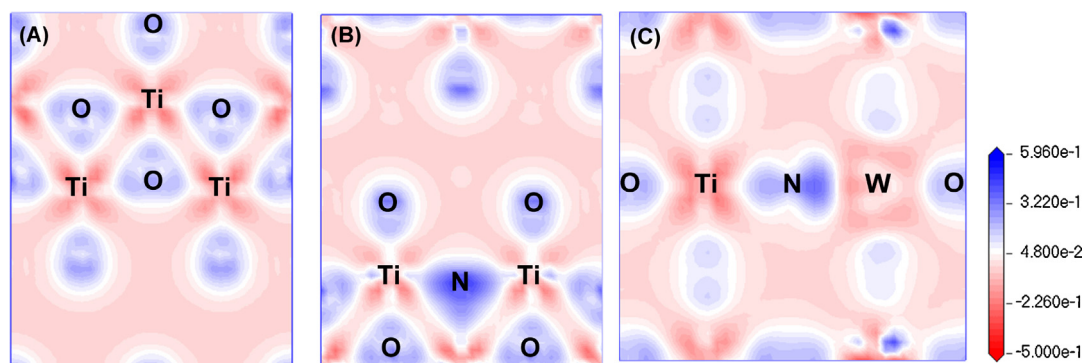


Fig. 10. Electron density differences among (A)  $\text{TiO}_2$ , (B)  $\text{N-TiO}_2$  and (C)  $\text{W/N-TiO}_2$  (showing only one plane).

inset of Fig. 9G. The presence of W inside the lattice of  $\text{W/N-TiO}_2$  affected the intermediate energy state, in which the physically larger atomic size of W occupied more volume than Ti, resulting in the distortion of Ti–N bond. The distortion of the Ti–N bond was proven by the reconstruction of the  $\text{W/N-TiO}_2$  lattice, in which the bond length and bond angle changed (Fig. 9H and I). The bond distance of W–N decreased to 1.789 Å, which was much shorter than that of N–Ti (1.950 Å) for  $\text{N-TiO}_2$ . Consequently, a strong W–N bond formed in  $\text{W/N-TiO}_2$ , resulting in increased bond angle of O–W–N ( $\angle\text{O4WN}$ ) (98.97°).

To further understand the transfer mechanism of electrons, electron density difference maps of  $\text{TiO}_2$ ,  $\text{N-TiO}_2$  and  $\text{W/N-TiO}_2$  were obtained, as shown in Fig. 10. Fig. 10B shows that in the case of  $\text{N-TiO}_2$ , the inclusion of N in the lattice resulted in a paramagnetic impurity and doublet ground state. A strong N 2p character was largely localized on N atom because of the high density of electrons. Fig. 10B also clearly shows electron transfers from Ti to the coordinated N. Therefore, greater charge depletion (accumulation) around Ti (N) can be obtained in  $\text{N-TiO}_2$  than in  $\text{TiO}_2$  (Fig. 10A), resulting in the distortion of bonds in the lattice of  $\text{N-TiO}_2$ .

In  $\text{W/N-TiO}_2$  (Fig. 10C), electron density was more localized on N than W atom. A covalent bond formed between W and N atoms, indicating that N formed a stable eight-electron shell with no unpaired electron. Long et al. [64] pointed that the unpaired electron of N inside  $\text{W/N-TiO}_2$  forms a new bond with W because of the higher Bader charges [65,66] of  $\text{W/N-TiO}_2$  than  $\text{N-TiO}_2$ . Charge imbalance between  $\text{W}^{6+}$  and  $\text{N}^{3-}$  ions inside the lattice may have occurred, as clearly shown in the surrounding electrons of N atom in Fig. 10C. Consequently, an electric dipole between W and N atoms forms. The dipole moment also causes an internal local polarization field that improves the separation of photogenerated holes and electrons, which plays a key role in photocatalysis [67,68].

#### 4. Conclusions

$\text{N-TiO}_2$  and  $\text{W/N-TiO}_2$  nanoparticles were successfully prepared to serve as photocatalysts for the PC degradation of pollutants and hydrogen evolution by an easy hydrothermal process. As expected, the PC efficiency for pollutant degradation increased, and hydrogen evolution with  $\text{W/N-TiO}_2$  (W0.1%–N1 g- $\text{TiO}_2$ ) exhibited improved PC activity. The degradation efficiency of methyl orange increased to 69% on W0.1%–N1 g- $\text{TiO}_2$  under visible light illumination, which is almost 5.3 and 1.25 times higher than that for  $\text{TiO}_2$  and  $\text{N-TiO}_2$  (N1 g- $\text{TiO}_2$ ), respectively. In addition, the PC rate for hydrogen production increased to  $0.2913 \text{ min}^{-1}$  after visible light irradiation, which is about 1.48 times higher than that for  $\text{N-TiO}_2$  (N1 g- $\text{TiO}_2$ ). The high PC efficiency of  $\text{W/N-TiO}_2$  can be mainly attributed to the new intermediate states. DFT calculations indicated that the hybridization between N 2p and O 2p led to the formation of intermediate energy responsible for

the high PC activity of  $\text{N-TiO}_2$ . Formation of an N–W–O bond and a polarization field between W and N atoms improved the PC activity of  $\text{W/N-TiO}_2$ . All calculation results rationalized the experimental observations on enhanced PC activity.

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